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Investigations on Linear and nonlinear properties of newly synthesised potassium hydrogen phthalate magnesium sulphate crystal – A promising third order NLO crystal

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ABSTRACT

A remarkably good second and third-order nonlinear optical (TONLO) single crystal potassium hydrogen phthalate magnesium sulfate (KHPMS) has been grown effectively using aqueous solution by conventional solution growth method. Single crystal XRD studies exhibits the crystal structure as triclinic with space group $P\bar{1}$ for the grown KHPMS crystal. Crystalline nature of the title compound has been confirmed by powder XRD studies and by using Scherer formula particle size has been evaluated. Elemental analysis with CHNS mode authenticates the occurrence of carbon, hydrogen and sulphur in the grown crystal. The optical transmission study proves the transparency of the sample in the entire visible region and band gap has been determined using Tauc's plot. The output intensity of SHG was verified by Kurtz and Perry powder technique and it was found to be 0.409 times as that of KDP. TONLO properties such as nonlinear refraction (NLR), nonlinear absorption (NLA), third-order susceptibility (χ^3) and hyperpolarizability (γ) were calculated with high accuracy using Z-scan technique.THG effectively attributes to self-defocusing effect with high third-order susceptibility compared with other NLO crystals.

Keywords: Crystal growth, optical, NLO, Z-scan, THG, susceptibility.

INTRODUCTION

The importance of finding new materials with large nonlinear properties has been increased intensively, due to the numerous and variable applications in various fields such as frequency conversion, high-speed information processing, telecommunications, optical data storage, photonic devices, such as optical limiter [1,2]. Compared with organic NLO materials, semi-organic materials has extended transparency region-down to UV, chemical inertness, large non-linearity, high resistance to laser induced damage, low angular sensitivity, and good mechanical hardness [3]. The semi organic NLO materials merge good traits of both organic and inorganic materials.

Crystals of phthalic acid derivatives are potential candidates for NLO and electro-optic processes [4]. Potassium hydrogen phthalate (monoacid potassium phthalate or KAP), is a biaxial crystal with non-centrosymmetic in nature, can be grown easily. It is widely used in x-ray monochromate and x-ray analyzer [5-8]. KAP is extensively studied for its crystal morphology. Epsomite, is a widespread evaporate material and has played a number of roles in scientific studies over the last four decade. It is a hydrogen bonded single crystal having wider medical and pharmaceutical applications. It is reported that optical quality of the crystal improves on doping with KCl [9]. So our attention has been drawn towrds mixing peculiar combination of potassium hydrogen pthalate with epsomite. According to keen literature survey no report has been made for this combination. In this present work we have made an attempt to grow and explore spectral, optical, linear, second and third order NLO properties in detail.

SYNTHESIS

KHPMS crystal was synthesized by combining analytical reagents (ARgrade), potassium hydrogen pthalate and magnesium sulphate in the molar ratio 1:1 with distilled water as a solvent. The growth was carried out by the slow evaporation method at room temperature. The prepared solution was vigorously stirred for 8h. Continuous stirring slightly increases in temperature ensures homogeneity and avoids the coprecipitation and motifs. The saturated solution was prepared and filtered to remove insoluble impurities. This synthesized clean solution was poured inta a Petri dish and covered with polythene paper with pores, which allowed for slow evaporation of the water solvent. After a duration of 3 weeks, the solvent had evaporated and good quality KHPMS crystals with dimensions of 0.2 × 0.2 × 0.1 cm^3 were harvested from the petric dish. The as-grown was of good quality, transparent and it is depicted in Figure 1. The synthesized KHPMS crystal was obtained based on the following chemical reaction:

$C_8H_5KO_{4+}MgSO_4.7H_2O \longrightarrow (C_8H_4O_3K).MgSO_4 + 7H_2O \uparrow$

Potassium hydrogen phthalate+magnesium sulphate ⟶ KHPMS crystal

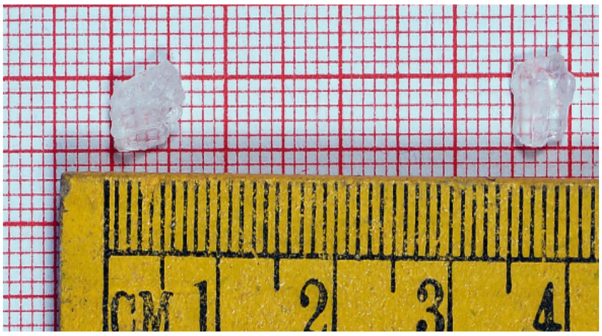

Figure 1: Photograph of as grown crystal

RESULTS AND DISCUSSION

Single X-ray diffraction study

The single crystal X-ray diffraction (XRD) analysis was carried out using Bruker X8 Kappa APEXII spectrometer (USA). Single crystal XRD indicates that the grown crystal belongs to triclinic crystal system with centrosymmetic space group $P\bar{1}$ which is in very good agreement with the reported literature listed in Table 1 [10]. The centrosymmetric is one of the key factor satisfying essential material requirements for SHG and THG activity of the crystal.

Table 1: Single crystal x-ray diffraction data of KHPMS crystal

Crystal	Lattice parameters			Interfacial angles			V	Crystal system	Space group
	(Å)						(Å³)		
	a	b	c	α	β	γ			
KHPMS	6.83	10.27	30.99	82.0°	89.7°	89.2°	2157	triclinic	$P\bar{1}$

Powder X-ray diffraction studies

The synthesised material were subjected to powder XRD using D8 advance and Bruker X-ray diffract meter with $CuK_\alpha 1$ radiation (λ=1.5406Å) studies, to analyze whether the synthesized material is crystalline or amorphous. The powder X-ray diffraction pattern of KHPMS is shown in Figure 2 where many diffraction peaks confirms the crystalline nature of the synthesised compoud. The average grain of the KHPMS were calculated using Scherer's equation:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

β is the half high width of the diffraction peak of the sample then β=0.3, and

2θ=14°36' is the Braggs' angle (deg.) Then the average size of the particle is 28.59 nm.

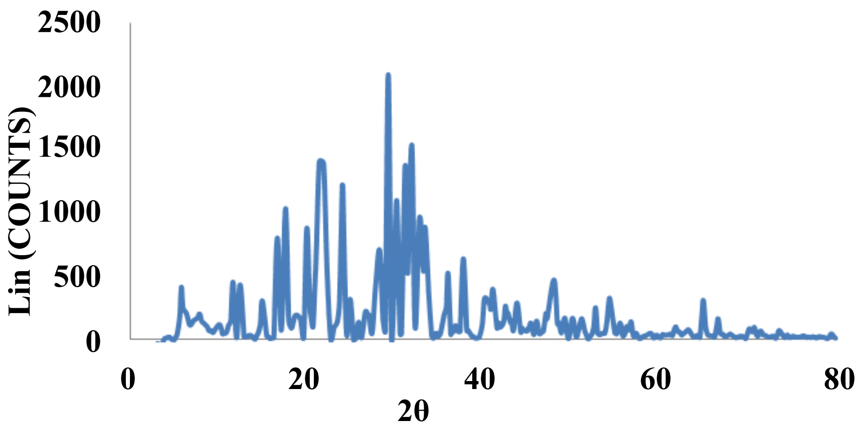

Figure 2: Powder XRD pattern of the title compound

Elemental analysis

Elemental analysis was carried using Elementar Vario EL111 with CHNS mode revealed, the presence of elements such as C=7.05%, H=5.83% N=7.05% and S=8.71% and also gives information about non-occurrence of N% in the above formed compound.

Optical transmission studies

The UV-VIS-NIR transmittance spectrum was assessed using PERKIN ELMER LAMBDA 35 UV winlab V 6.0 SpectrKHPMSter with its wavelength range of 175-2300 nm. The optical transmission spectra shown in Figure 3 specify that the crystal has a very high optical transparency of 99% with lower cut-off wavelength 317 nm, gratifying the prerequisite property of NLO material and making it more suitable for various optical and electronic applications [11-14]. The optical absorption coefficient (α) was premeditated from transmittance using the following relation:

$$\alpha = \frac{2.303}{d}\log\left(\frac{1}{T}\right) \quad (2)$$

Where, d and T are the sample thickness and transmittance respectively. The band gap of the crystal is estimated by using Tauc's relation [15],

$$\alpha = \frac{A(h\nu - E_g)^{\frac{1}{2}}}{h\nu} \quad (3)$$

Where, E_g is the optical band gap of the crystal and A is a constant independent of photon energy. By employing Tauc's plot in Figure 4, drawn between $(\alpha h\nu)^{1/2}$ and hν representing the direct band gap nature of the crystal and by extrapolating the linear portion near the commencement of absorption edge to x-axis, the band gap is measured to be 3.85 eV in accordance with the theoretical band gap value 3.9 eV calculated by, $E_g = \frac{1240}{\lambda}$ eV, (λ is 317 nm). The widespread band gap of KHPMS crystal authorizes the high optical transmittance in the entire visible region, as it can permit electro-optic applications [16].

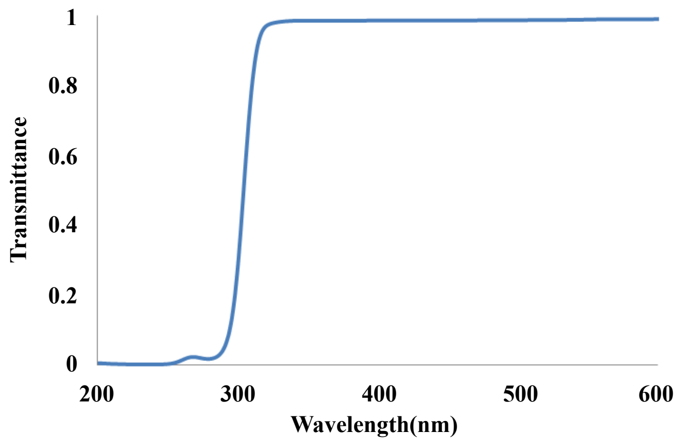

Figure 3: Transmission spectrum of the grown crystal KHPMS

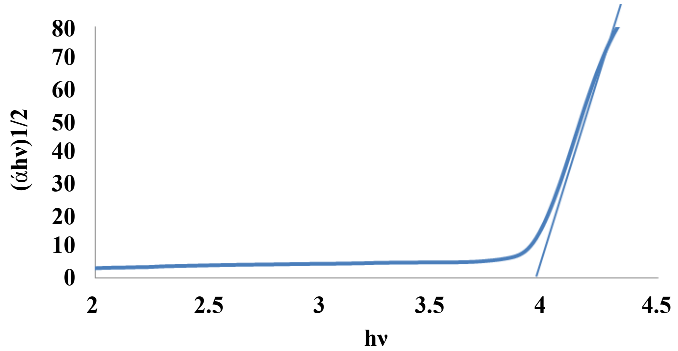

Figure 4: Touc's Plot of KHPMS

Second-order nonlinear studies

The second harmonic generation efficiency of KHPMS crystal was measured by Q switched High Energy Nd: YAG Laser (QUANTA RAY Model LAB-170-10).

With reference to Kurtz-Perry powder SHG technique with potassium dihydrogen phosphate (KDP) crystal as reference material [17]. The fundamental laser beam of 1064 nm wavelength and 8 ns pulse width, with 10 Hz pulse rate, was made to fall normally on the sample cell. The input laser energy incident on the powdered sample was chosen to be 5.65 mJ/pulse. The grown single crystal of KHPMS and reference KDP was ground in a uniform particle size of 125-150 m, packed in a micro capillary of uniform bore size, and exposed to laser radiations. The fundamental beam was filtered by using an IR filter. A photomultiplier tube was used as detector. The output from the sample was monochromated to collect the intensity of 532 nm component and to eliminate the fundamental radiation. The generation of the second harmonic was confirmed by the emission of green light. The SHG output efficiency for KHPMS and KDP samples was found to be 0.524 and 1.27, respectively. Thus, it is observed that even though KHPMS crystal is a centrosymmetric crystal, it exhibits SHG property and its efficiency was found to be 0.412 times as that of KDP.

Third order non-linear optical properties

Z-scan method is a typical and simple technique widely accepted by non-linear community for the accurate measurements of third order nonlinear properties like nonlinear susceptibility χ^3, nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) etc. In this Z-scan experiment He-Ne laser of wavelength 632.8 nm with beam diameter 1cm is used to scan the sample. The sample was fine-tuned on a holder 90° and it is moved along the negative (-Z) to positive (+Z) axis, which is the direction of propagation of the laser beam. The translation of sample table can be controlled by computer for precision of each movement. The corresponding transmitted intensity through the sample was accumulated by a photo-detector and it is deliberated by the digital power meter. The experimental set up for open and closed aperture was depicted in the Figure 5.

Figures 6a and 6b shows the closed and open aperture of Z-scan data for KHPMS crystal. In the present study closed aperture (CA) shows the peak followed by a valley transmittance which is the signature for negative nonlinearity. This is known as self-defocusing effect which is due to local variation of refractive index with temperature. Hence KHPMS can be employed in the protection of night vision sensors [18] due to their negative nonlinear refraction property "which also given in Table 2".

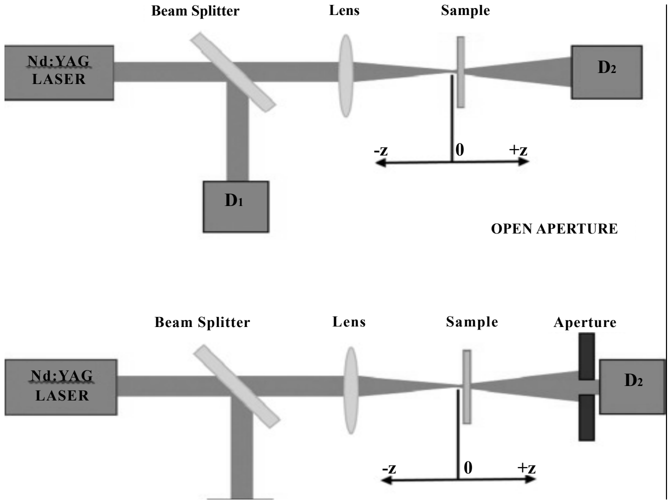

Figure 5: Experimental set for Z-scan technique

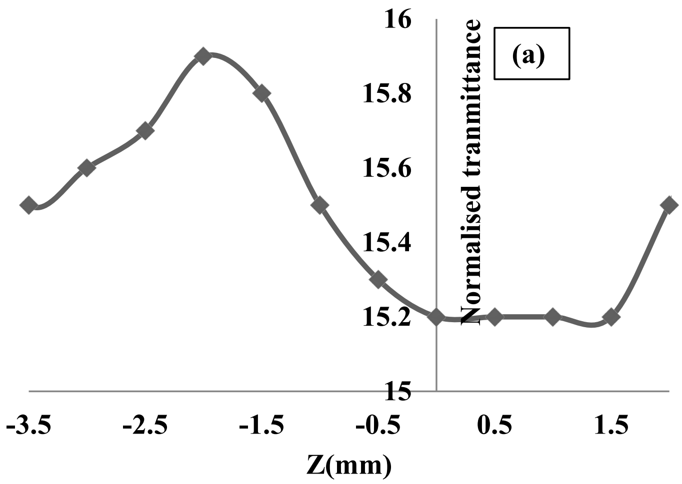

Figure 6a: The closed aperture of Z-scan study for KHPMS crystal, respectively

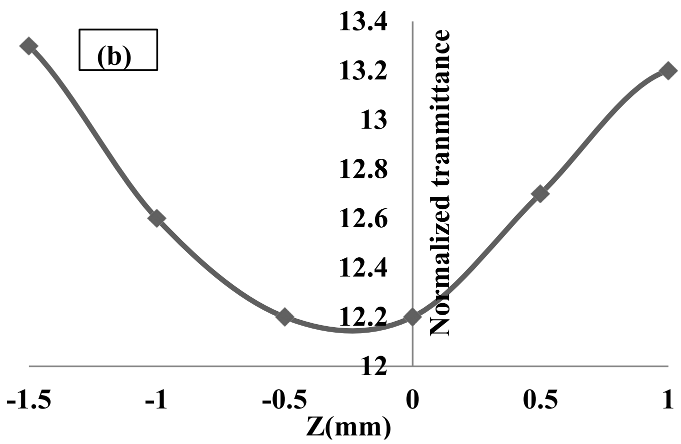

Figure 6b: The open aperture of Z-scan study for KHPMS crystal, respectively

In order to find out the non-linear refractive index (n_2) of KHPMS crystal, the difference between the transmittance peak and valley transmission can be written in terms of the axis phase shift given by Saltiel et al. [19],

$$\Delta T_{p-v}=0.406(1-S)^{0.25}|\varphi| \quad (4)$$

Where, S is the aperture linear transmittance and is calculated using the following equation:

$$S=1-\exp\left(\frac{-2r_a^2}{\omega_a^2}\right) \quad (5)$$

Where, r_a is the radius of the aperture and ω_a is the spot size diameter in front of the aperture, the non -linear refractive index is given by the relation:

$$n_2=\frac{\varphi}{KI_{0L_{eff}}} \quad (6)$$

Where, K=2π/λ (where λ is the laser wavelength), I_0 is the input intensity, Z=0 and $L_{eff}=\left[\frac{1-\exp(-\alpha L)}{\alpha}\right]$, L_{eff} is the effective thickness of the sample and α is the linear absorption coefficient of the KHPMS crystal. From the open aperture Z-scan data (OA) the non-linear absorption co-efficient [20] is estimated as:

$$\beta=\frac{2\sqrt{2}\Delta T}{I_o L_{eff}} \quad (7)$$

Where, ΔT is the one valley at the open aperture Z-scan curve.

For the title compound the value of β found to be negative leads to saturable absorption. The real and imaginary parts of the third order non-linear optical susceptibility χ^3 are defined by the equations [21]:

$$(\text{Re}\,\chi^{(3)})\,(\text{esu})=\frac{10^{-4}\left(\varepsilon_0 c^2 n_0^2 n_2\right)}{\pi}\,(\text{cm}^2/\text{W}) \quad (8)$$

$$(\text{Im}\,\chi^{(3)})\,(\text{esu})=\frac{10^{-4}\left(\varepsilon_0 c^2 n_0^2 \beta\lambda\right)}{4\pi^2}\,(\text{cm}^2/\text{W}) \quad (9)$$

Where ε_0 is the vacuum permittivity (8.8518 × 10^{-12} F/m^2), c is the velocity of light in vacuum (3 × 10^8 m/s), n_0 is the linear refractive index of the sample and λ is the wavelength of laser beam used (632.8 nm). The third order nonlinear optical susceptibility of the crystal is calculated using the expression:

$$\chi^{(3)}=\sqrt{\left(\text{Re}\,\chi^{(3)}\right)^2+\left(\text{Im}\,\chi^{(3)}\right)^2} \quad (10)$$

The comparision of third order susceptibilities KHPMS with other NLO crystals were listed in Table 3, found to be greater than other NLO crystals, Hence, overall results signature that, the grown KHPMS crystal contains better NLO response, and it might be considered as a favourable candidate for optical data processing, optical logic gate, optical limiting and all-optical switching device applications.

Table 2: Experimental details and the results of Z-scan technique

Parameters	**KHPMS**
Laser beam wavelength (λ)	632.8 nm
Power of laser (P)	25 µW
Lens focal length (f)	18.5 cm/8.5 cm
Optical path length (Z)	115 cm
Spot size diameter in front of the aperature (ω_a)	1 cm
Aperature radius (r_a)	2 mm
Sample thickness (L)	2.28 mm
Effective thickness (L_{eff})	2.54 × 10^{-3} mm
Linear absorption co-efficient (α)	1.9667
Non-linear refractive index (n_2)	-2.23 × 10^{-10} cm^2/W

Non-linear absorption co-efficient (β)	4.48×10^{-3} cm/W
Real part of the third susceptibitlity (Re $\chi^{(3)}$)	-8.42×10^{-10} esu
Imaginary parta of the third-order susceptibility (Im $\chi^{(3)}$)	8.528×10^{-7} esu
Third-order non-linear optical susceptibility $\chi^{(3)}$	8.42×10^{-10} esu

Table 3: Comparison of third order susceptibility ($\chi^{(3)}$) values of KHPMS crystal with other NLO crystals [22-27]

Crystal	Third order susceptibility ($\chi^{(3)}$)
KHPMS	8.42×10^{-10} esu
DMAPHB	1.016×10^{-13} esu
4Br4MSP	1.65×10^{-14} esu
KDP	4.0×10^{-14} esu
VMST	9.69×10^{-12} esu
$KBe_2BO_3F_2$	9.99×10^{-13} esu

CONCLUSION

Optically good quality single crystal potassium acid phthalate magnesium sulphate (KHPMS) of dimensions 0.2 × 0.2 × 0.1 cm^3 were grown within a period of three weeks by slow evaporation technique under room temperature. The grown crystal was subjected to single crystal x-ray diffraction analysis, band gap for the grown crystal was found to be 3.9 eV. Powder XRD study reveals the crystalline nature of the grown crystal. CHNS analysis authenticates the presence of C, H and N & S % in the synthesized compound. SHG efficiency of KHPMS crystal was found to be 0.412 times as that of KDP. Z-scan experimental result confirms the relatively large value of nonlinear optical absorption (β) and refractive index (n_2) and hence KHPMS crystal has large value of third order nonlinear susceptibility $\chi^{(3)}$ of 8.42×10^{-10} esu compared with other NLO crystals, which is most suitable for optical limiting applications. All these studies reveal that the KHPMS crystals are considered as potential candidates for the fabrication of electro-optic, nonlinear optical and optoelectronic devices.

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REFERENCES

[1] Anand, D.P., et al., *Mater Chem Phys*, **2006**. 97: p. 501-505.

[2] Shirsat, M.D., et al., *Cryst Res Technol*, **2008**. 43: p. 756-761.

[3] Hussaini, S.S, *J Opt Elect Adv Mater*, **2007**. 1: p. 707-711.

[4] Ganesh, R.B., *J Cryst Growth*, **2005**. 282: p. 429-433.

[5] Belyeav, L.M., et al., *Sov Phys Crystallogr*, **1970**. 14: p. 544.

[6] Hottenhuis, M.H.J. and Lucasiu, C.B., *J Cryst Growth*, **1986**. 78: p. 379-388.

[7] Hottenhuis, M.H.J. and Lucasiu, C.B., *J Cryst Growth*, **1988**. 78: p. 623-631.

[8] Hottenhuis, M.H.J. and Lucasiu, C.B., *J Cryst Growth*, **1989**. 78: p. 708-720.

[9] Ferdous, S. and Podder, J., *J Bangladesh Acad Sci*, **2009**. 33(1): p. 47-54.

[10] Kariuki, B.M. and Jones, W., *Acta Crystallogr C*, **1989**. 45(9): p. 1297-1299.

[11] Joseph, C. and Ittyachen, M.A., *Mater Lett*, **2001**. 49(5): p. 299-302.

[12] Venkataramanan, V., et al., *J Cryst Growth*, **1997**. 179(3): p. 605-610.

[13] Eya, D.D.O., Ekpunobi, A J. and Okeke, C.E., *Acad Open Internet J*, **2006**. 17: p. 1-10.

[14] Pandey, V., *J Optoelectron Adv Mater*, **2005.** 7: p. 2641-2646.

[15] Tauc, J., Grigorovici, R. and Vancu, A., *Phys Status Solid*, **1966**. (b)15.2: p. 627-637.

[16] Rajesh, P. and Ramasamy, P., *J Cryst Growth*, **2009**. 311(13): p. 3491-3497.

[17] Kurtz, S.K. and Perry, T.T., *J Appl Phys*, 1968. 39(8): p. 3798-3813.

[18] Pabitha, G. and Dhanasekaran, R., ***Opt Laser Technol*, 2013**. 50: p. 150-154.

[19] Saltiel, S., Tanev, S. and Boardman, A.D., *Opt Lett*, **1997**. 22(3): p. 148-150.

[20] Sheik-Bahae, Mansoor, et al. *IEEE J Quantum Electron*, **1990**. 26(4): p. 760-769.

[21] Stryland, E.W.V and Sheik-Bahae, M. Z-scan measurements of optical nonlinearities, **1998**. 18(3): p. 655-692.

[22] D'silva, E.D., et al. *Mater Res Bull*, **2012**. 47(11): p. 3552-3557.

[23] Duanliang, W., et al., *RSC Adv*, **2016**. 6(18): p. 14490-14495.

[24] Kumar, M.K., et al., *Opt Mater*, **2014**. 36: p. 988 -995.

[25] Li, F.Q., et al., *Appl Phys B*, **2012**. 108: p. 301-305.

[26] Sathya, P., Pugazhendhi, S. and Gopalakrishnan, R., *RSC Adv*, **2016**. 6(50): p. 44588-44598.

[27] Nalla, V., et al., *IUCrJ*, **2015**. *2*(3): p. 317-321.